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Quantitative Analysis of Aqueous NO_2^--NO_3^- Solutions by Infrared Internal Reflection Spectroscopy

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QUANTITATIVE ANALYSIS OF AQUEOUS NO_2^--NO_3^- SOLUTIONS BY INFRARED INTERNAL REFLECTION SPECTROSCOPY

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Abstract

Infrared spectra of aqueous NO_2^- and NO_3^- solutions, and of binary mixtures, were recorded using internal reflection techniques and a Fourier transform spectrometer. NO_2^- could be detected at a concentration of 0.02 M, and NO_3^- at 0.001 M. However, NO_3^- also became adsorbed on the Ge prism. After making corrections for NO_3^- adsorption and for overlapping of NO_2^- and NO_3^- bands, it was possible to analyze binary mixtures with concentrations as low as $[NO_3^-] = 0.03$ M and $[NO_2^-] = 0.05$ M. By adjusting the optics so that the usually totally absorbing water stretching band had a transmittance of about 50%, it was possible to observe N-H and C-H stretching bands of solutes. Dissolved materials cause the water structure and consequently the water absorption to change, causing distortions of the background of ratioed spectra of aqueous solutions. These distortions may influence qualitative and quantitative observations.

The utility of infrared internal reflection spectroscopy (IRS) in providing information about adsorption from organic solvent at the liquid-solid interface (1) led us to attempt to study adsorption from aqueous solution, using a Ge IRS prism as adsorbent as well as for optical purposes. It was found that NO_3^- became adsorbed on Ge, prompting us to examine the quantitative aspects of the infrared

analysis of aqueous solutions of NO_3^-, NO_2^-, and of NO_3^--NO_2^- mixtures.

IRS analysis of aqueous $NaNO_3$ solutions has been described by Katlafsky and Keller (2), who found a linear variation, $[NO_3^-] = aA_{NO_3^-}$, of the 1335-cm^{-1} NO_3^- absorbance over the 5-20% concentration range. $A_{NO_3^-}$ is the NO_3^- absorbance. Wilhite and Ellis (3), using IRS, reported a similar linear variation for the 0.1-1 M NO_3^- range, but another linear relation, $[NO_3^-] = b + cA_{NO_3^-}$, for the 0.01-0.1 M NO_3^- range. Ahlijah and Mooney (4) used IRS to analyze aqueous $NaNO_3$-$NaNO_2$ solutions; their calibration plots were linear but their graphs (5) show them to be $[NO_3^-] = d + eA_{NO_3^-}$ and $[NO_2^-] = f + gA_{NO_2^-}$. Values of d and f are near 0.08 and 0.1 absorbance. As our observations differ somewhat from those made earlier, and the method is of potential utility, we describe our IRS study of aqueous NO_3^+, NO_3^-, and NO_3^--NO_2^- solutions.

EXPERIMENTAL

A Ge single-pass plate, 1 mm thick, was used in conjunction with a suitable variable-angle attachment described elsewhere (1). Spectra having a constant resolution of 8 cm^{-1} were recorded with a modified Digilab, Inc. Model FTS-14 Fourier transform spectrometer (6). All single-beam spectra were obtained by summing 400 interferograms. After the cell containing the Ge plate was installed, the sampling compartment was flushed with dry air. The cell remained in place throughout a series of measurements so that its transmission remained constant; small changes in cell position can cause transmission changes which can affect the results obtained when two single-beam spectra are ratioed. Pure water or solutions of various NH_4NO_2, NH_4NO_3, $NaNO_3$, $NaNO_2$, or $NaNO_3$ + $NaNO_2$ concentrations, prepared from distilled water and reagent-grade chemicals,

were placed into the cell or were withdrawn from it by means of syringes and Teflon tubing permanently attached to the cell.

RESULTS AND DISCUSSION

Only single-beam spectra were measured. These were stored by the instrument's disc memory, retrieved, and ratioed by computation as required, using the instrument's digital computer. Some examples of single-beam spectra are shown in Fig. 1. The equivalent penetration depth (7), computed by taking the molar extinction coefficient of liquid water to be 81 at 3450 cm^{-1} (8), was 3.1 μ at 3450 cm^{-1} and about 8 μ at 1600 cm^{-1}. Spectrum A is the "background" of the Ge plate in air. There were prominent CO_2 bands, and some water vapor bands in the 1900-1400 cm^{-1} region, caused by residual water vapor in the spectrometer. When water was in contact with the Ge plate, the prominent OH stretching and deformation bands were superimposed on the background (B, Fig. 1). The single-beam spectra of dilute solutions (C,D, Fig. 1) are similar to the spectrum of water; the bands of the solute are not prominent. The instrument function was removed when two such single-beam spectra were ratioed. If the empty cell was used as reference, the ratioed spectra had the appearance of spectra obtained by the usual double-beam operation, e.g. A, B, Fig. 2. Using water as the reference, the ratioed spectra had the appearance of double-beam, solvent-compensated spectra (C,D, Fig. 2). The slight CO_2 bands which appeared in some spectra were brought about by changes in the efficiency of the air dryer. The noise above 3000 cm^{-1} and below 1000 cm^{-1} in spectra C and D of Fig. 2 was the result of ratioing spectra in regions where the transmission was very low. In spectrum C, the negative OH stretching band, the negative OH deformation band, and the increase in absorption below 1000 cm^{-1}, which are barely detectable in

spectrum D, are not artifacts. These changes were caused by variations in the absorptivity of the water present in the solution, the water structure being affected by the solutes.

The absorptions of NO_3^- and NO_2^-, barely detectable in the single-beam spectra, became more recognizable in the ratioed spectra (A,B, Fig. 2); computer-produced scale expansion then made the bands usable. Examples are shown in Fig. 3. Trace A of that figure was obtained by recording two single-beam spectra of water and ratioing them against one another, in order to obtain an estimate of the noise level; it can be taken as a "100% line." Spectrum B shows the NO_3^- and NO_2^- bands. Spectrum C is a highly scale-expanded segment of spectrum D of Fig. 2, plotted to the same scale as spectrum C of Fig. 3; the noise level is consequently higher.

The ratioing and scale-expansion techniques outlined were used to examine single and binary solutions of various concentrations. Some segments of spectra of NH_4NO_2 solutions are shown in Fig. 4. Similar results were obtained with $NaNO_2$ solutions, the intensity of the 1237-cm^{-1} NO_2^- band decreasing progressively with decreasing NO_2^- concentration. A reasonably linear relation between the absorbance of the 1237-cm^{-1} band and NO_2^- concentration was obtained (Fig. 5). The lowest concentration yielding a usable spectrum was 0.02 M.

Similar measurements were carried out with NO_3^- solutions. Some results obtained with $NaNO_3$ are shown in Fig. 6. The intensity of the NO_3^- band decreased progressively as the NO_3^- decreased, but remained constant at concentrations less than 0.001 M (Fig. 6A).

With relatively concentrated solutions the NO_3^- band was broad and had a maximum at 1352 cm^{-1} and a shoulder near 1400 cm^{-1} (Fig. 6B). (The weak symmetric stretching band of NO_3^- could also be observed near 1050 cm^{-1} with 1 M NO_3^- solutions.) When the NO_3^- concentration declined, the 1400-cm^{-1} absorption diminished and the

maximum of the residual, sharp band shifted to 1350 cm^{-1}. The NO_3^- band of the more concentrated solutions is more like that of solid $NaNO_3$, for which the asymmetric stretching band is at 1374 cm^{-1} (9).

The sharp residual NO_3^- band, which could not be diminished by extensive flushing with water but which could be removed by treating the Ge plate with hot chromic acid cleaning solution, is attributed to an NO_3^- species fairly strongly bound to the Ge surface. Using the absorbance of the residual peak, and assuming that the species causing the band was NO_3^-, and that the area of the Ge plate was 20 cm^2, leads to an estimate of one adsorbed unit per 5-10 $Å^2$ of surface.

The total NO_3^- absorbance at 1352 cm^{-1} could be corrected by subtracting the absorbance of the residual band of the adsorbed material. When this was done, the absorbance of NO_3^- in solution was found, and a reasonably linear relation between the corrected absorbance values and NO_3^- concentration was obtained (Fig. 5). From t + plot, the absorbance of the residual band (0.0111) is equivalent to the absorbance of ~0.05 M NO_3^- solution. Using the extinction coefficient of NO_3^- for the adsorbed species and estimating an equivalent penetration depth of about 7 μ at 1350 cm^{-1} leads to an estimate that the absorbance of the adsorbed species was equivalent to the absorbance of a solution of about 0.06 M NO_3^-, in fair agreement with the value obtained from the NO_3^- calibration curve.

However, the calibration plots of Fig. 5 cannot be used directly for estimating the concentrations of NO_3^--NO_2^- mixtures. The 1237-cm^{-1} NO_2^- band (asymmetric stretching) has a shoulder at 1340 cm^{-1} (symmetric stretching) which, as shown clearly by Fig. 7, overlapped the 1352-cm^{-1} NO_3^- band. The latter does not cause the

absorbance of the 1237-cm^{-1} NO_2^- band to change significantly. The ratio of the absorbance at the 1340-cm^{-1} shoulder and that of the 1237-cm^{-1} band is about 4:21. Taking the ratio of the absorbances of the NO_2^- asymmetric and symmetric stretching bands to be constant then gives

$$\left[\begin{array}{c}\text{absorbance at 1352 cm}^{-1}\\ \text{due to NO}_3^-\end{array}\right]=\left[\begin{array}{c}\text{total absorbance}\\ \text{at 1352 cm}^{-1}\end{array}\right]-\left[\frac{\text{absorbance at 1237 cm}^{-1}}{5.25}\right]$$

Some results obtained with dilute solutions are summarized in Table 1. The correction for NO_3^- has been made. The agreement between "actual" and "found" values is not unreasonable. If the correction for the band overlapping had not been made, the NO_3^- concentration values would have been too high by about 1/5th of the concentration of NO_2^-. It is pertinent to note that the lowest concentrations reported earlier (4) for a binary mixture were $[NO_2^-]$ = 0.7 M, $[NO_3^-]$ = 0.5 M, 14 and 17 times as great as the lowest values in Table 1.

There are considerable differences in the frequencies of the NO_3^- and NO_2^- absorptions which have been reported; a summary is given in Table 2. The dispersion of the index of refraction in the infrared region is known (7); i.e., in the vicinity of an absorption band, the index of refraction first decreases, then increases sharply, and decreases again to approach the normal value after the absorption has been passed. Consequently, with IRS, the penetration depth reaches a maximum when the index of refraction reaches a maximum. When the sine of the incident angle is very close to the ratio of the refractive indices, the absorption band maximum is distorted toward lower frequency.

In the present experiments, Ge and an average angle of incidence more than 60° were employed. The sine of the incident angle and the

refractive index ratio of the Ge and liquid are far apart (0.87 and 0.33). The effect of the dispersion of the refractive index of the aqueous solution on the absorption band positions was therefore negligible. However, Katlafsky and Keller (2) used an Irtran-2 plate with an incident angle of 40°. The critical angle for the system ZnS(Irtran-2)-H_2O in the infrared range is 37.5°. Consequently, the incident angle was quite close to the critical angle, and any dispersion of the refractive index would cause a shift of absorption band maxima. Similarly, Ahlijah and Mooney (4, 10) used a KRS-5 plate and stated that the incident angle was 30°. However, the critical angle for the KRS-5-H_2O system is 33.7°, the refractive index of KRS-5 and H_2O being taken as 2.4 (7) and 1.33, respectively. Their measurements must have been made with the incident angle close to the critical angle, so that, again, band distortions occurred. The low values of band positions reported by Katlafsky and Keller and by Ahlijah and Mooney can be attributed to band distortions caused by improper IRS techniques.

It was of interest to determine how well spectral features of dissolved materials could be discerned in the vicinity of the intense water stretching band. Consequently, the incident angle was adjusted to decrease the penetration depth to about 0.8 μ at 3400 cm^{-1}. The spectra of Fig. 8 were then recorded.

The water stretching band (A, Fig. 8), obtained at about 50% maximum transmittance, has the same contour as the band observed by transmission measurements by Thompson et al. (13). Two broad absorptions due to NH_4^+ (8) appear on the low-wavenumber side of the OH band in the 3100-2600 cm^{-1} region when NH_4NO_3 is dissolved in the water (B, Fig. 8), and these become more prominent when the spectra are solvent-compensated (C,D, Fig. 8) and then scale-expanded

(Fig. 9). There is, however, some distortion of the 3050-cm^{-1} band because of the negative OH band. The distortion decreases as the solute concentration is decreased, but this also decreases the solute bands. Consequently, as the liquid layer is necessarily thin as well as dilute, the signal-to-noise ratio decreases. With the present technique the lowest concentrations at which N-H and C-H bands (similar experiments were made with aqueous methanol, Na citrate, etc.) were observed were near 0.1 M.

The results thus show that it is feasible to obtain spectral information near or even at the position of one of the strong water absorptions. It must be kept in mind, however, that the presence of solutes causes the water bands to change in absorption, so that distortions result. Such distortions may also affect quantitative results by causing base lines to fluctuate. The distortions decrease in intensity with decreasing solute concentration. However, because their intensities and frequencies are a function of the nature of the solute, they cannot be precisely compensated.

Acknowledgment

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Table 1

Analysis of $NaNO_3$-$NaNO_2$ Solutions

M NO_2^- actual	M NO_3^- actual	M NO_2^- found	M NO_3^- found[a]
0.20	0.20	0.20	0.21
0.050	0.050	0.059	0.058
0.050	0.150	0.064	0.18
0.15	0.050	0.14	0.06
0.050	0.030	0.044	0.033

[a]Corrected for adsorption and band overlapping.

Table 2

Absorptions of $NaNO_2$ and $NaNO_3$

IRS			Transmission		
This Work	Katlafsky and Keller (2)	Ahlijah and Mooney (4)	(11)	(9,12)	Assignment
1352	1335	1333	1370	1385	NO_3^- asym. stretch
1047		1045	1050	1049	NO_3^- sym. stretch
1340		1316		1335	NO_2^- asym. stretch
1237	1225	1220		1240	NO_2^- sym. stretch

Figures

Fig. 1. Single-Beam Spectra

A: dry Ge plate in empty cell. B: water. C: aqueous solution 0.2 M in $NaNO_3$ and 0.2 M in $NaNO_2$. D: aqueous solution 0.03 M in $NaNO_2$ and 0.05 M in $NaNO_3$.

Fig. 2. Ratioed Spectra

Each spectrum shown was obtained by ratioing two of the spectra of Fig. 1. A: water (B, Fig. 1/A, Fig. 1). B: 0.2 M $NaNO_2$ + 0.2 M $NaNO_3$ solution (C, Fig. 1/A, Fig. 1). C: 0.2 M $NaNO_2$ + 0.2 M $NaNO_3$ solution (C, Fig. 1/B, Fig. 1). D: 0.03 M $NaNO_2$ + 0.05 M $NaNO_3$ solution (D, Fig. 1/B, Fig. 1).

Fig. 3. Scale-Expanded Spectra

A: "100% line"; see text. B: 0.2 M $NaNO_2$ + 0.2 M $NaNO_3$ solution; scale-expanded segment of spectrum B of Fig. 2. C: 0.03 M $NaNO_2$ + 0.05 M $NaNO_3$ solution; scale-expanded segment of spectrum D of Fig. 2.

Fig. 4. Spectra of NH_4NO_2 Solutions

The numbers next to each trace indicate the molar concentrations.

Fig. 5. Calibration Curves

Fig. 6. Spectra of $NaNO_3$ Solutions

The numbers next to each trace indicate $[NO_3^-]$ in M. All spectra are scale-expanded. Part A shows segments taken from a series of spectra, all spectra of the series being scale-expanded by the same factor; band intensity is consequently proportional to concentration. The same segments are shown again in Part B. In order to make changes in band contour more detectable, only the absorption in the 1550-1000 cm^{-1} range was expanded. For each segment, the lowest absorption within that range was placed at the bottom of the chart and the highest absorption at the top of the

chart, so that the peak heights are the same. The expansion factor is different for each segment and is supplied by the computer.

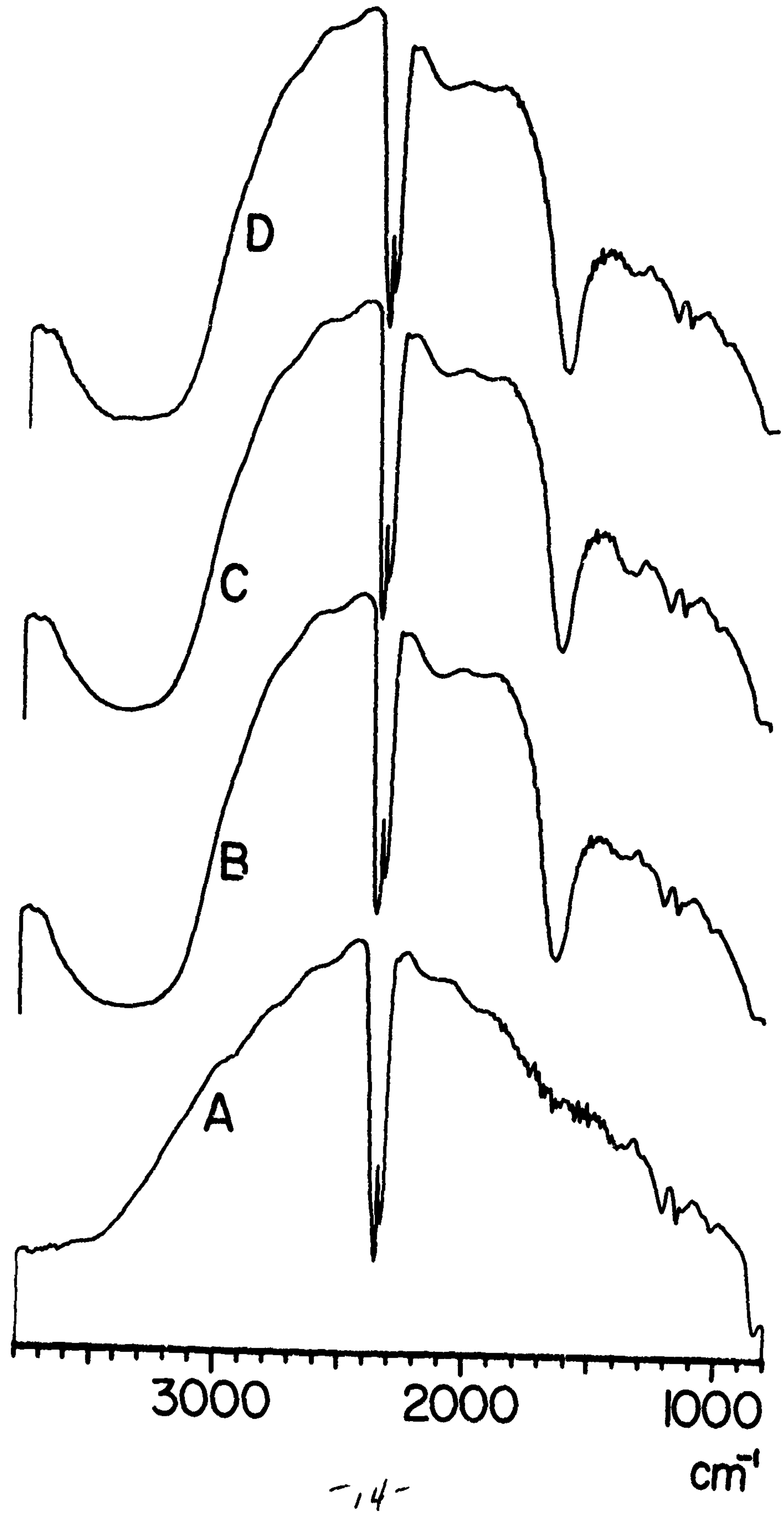
Fig. 7. Spectra of NO_3^- and NO_2^-

Fig. 8. Spectra of H_2O and NH_4NO_3 Solutions

A: water. B: 2 M NH_4NO_3 solution. The reference used for the ratioed spectra A and B was the single-beam spectrum of the dry Ge. C: 2 M NH_4NO_3 solution, the ratio of spectra B and A. D: 1 M NH_4NO_3 solution, the ratio of a spectrum (of 1 M NH_4NO_3 solution similar to spectrum C) and spectrum A.

Fig. 9. Spectra of NH_4^+

Scale-expanded segments of spectra C and D of Fig. 8.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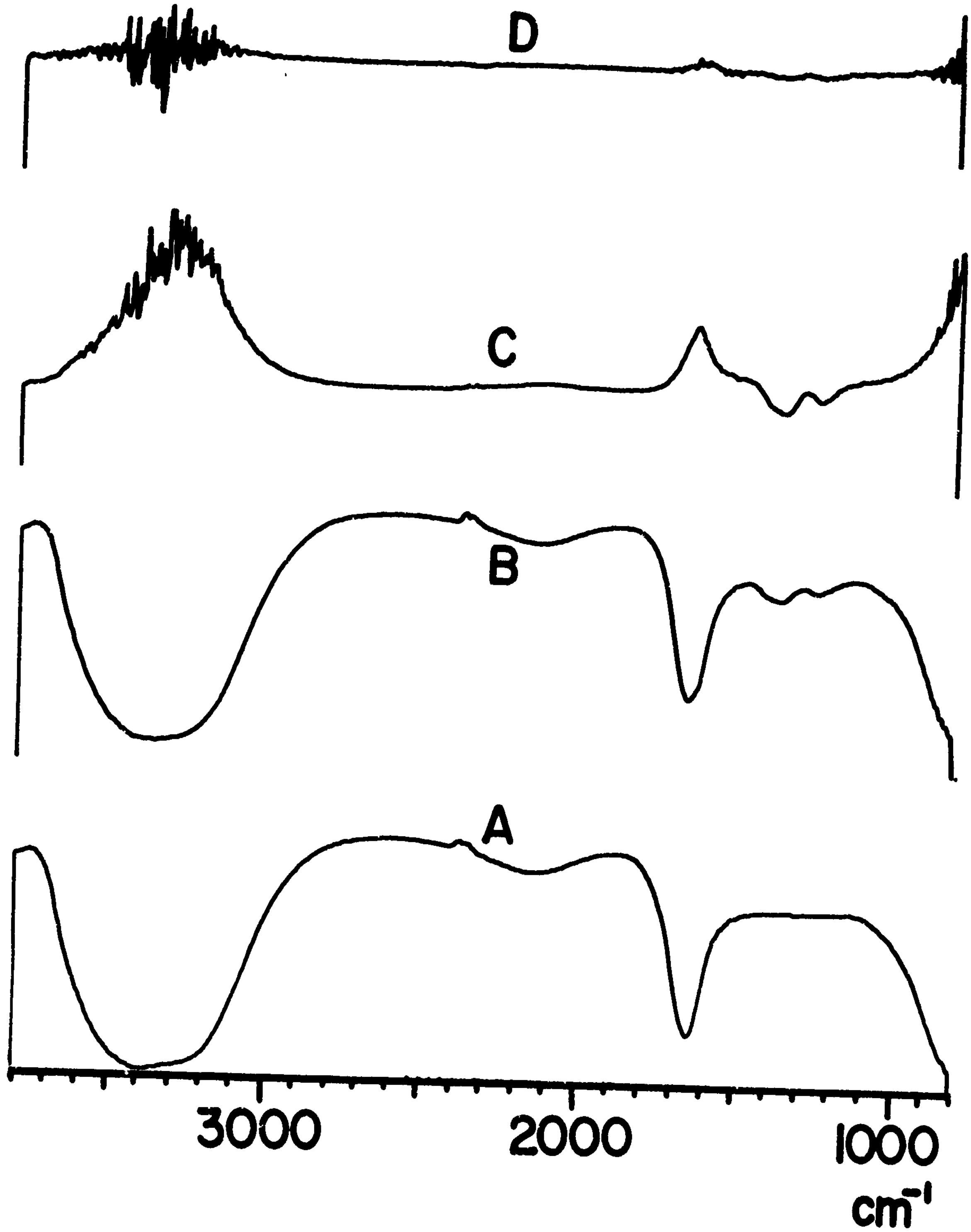

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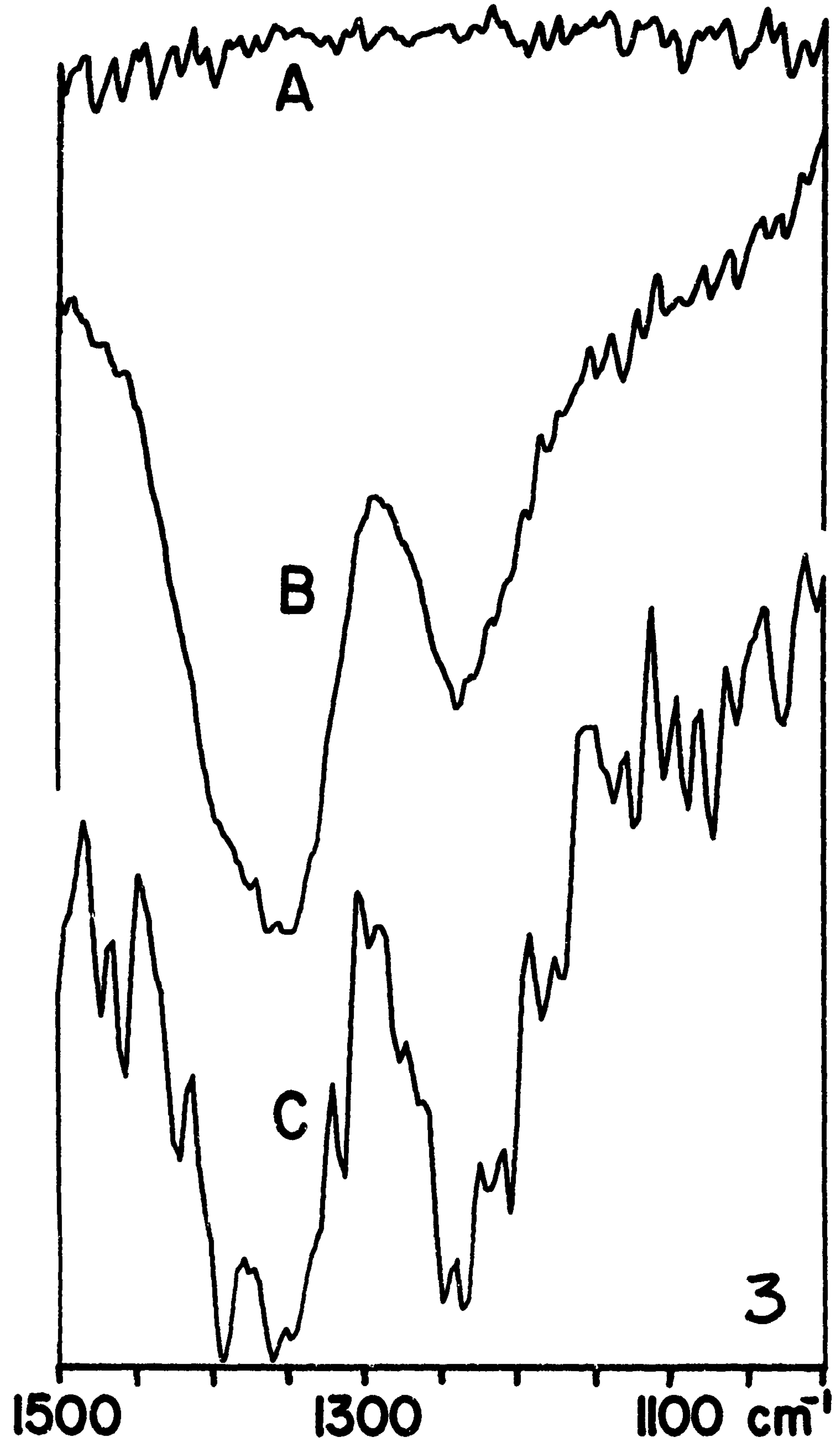
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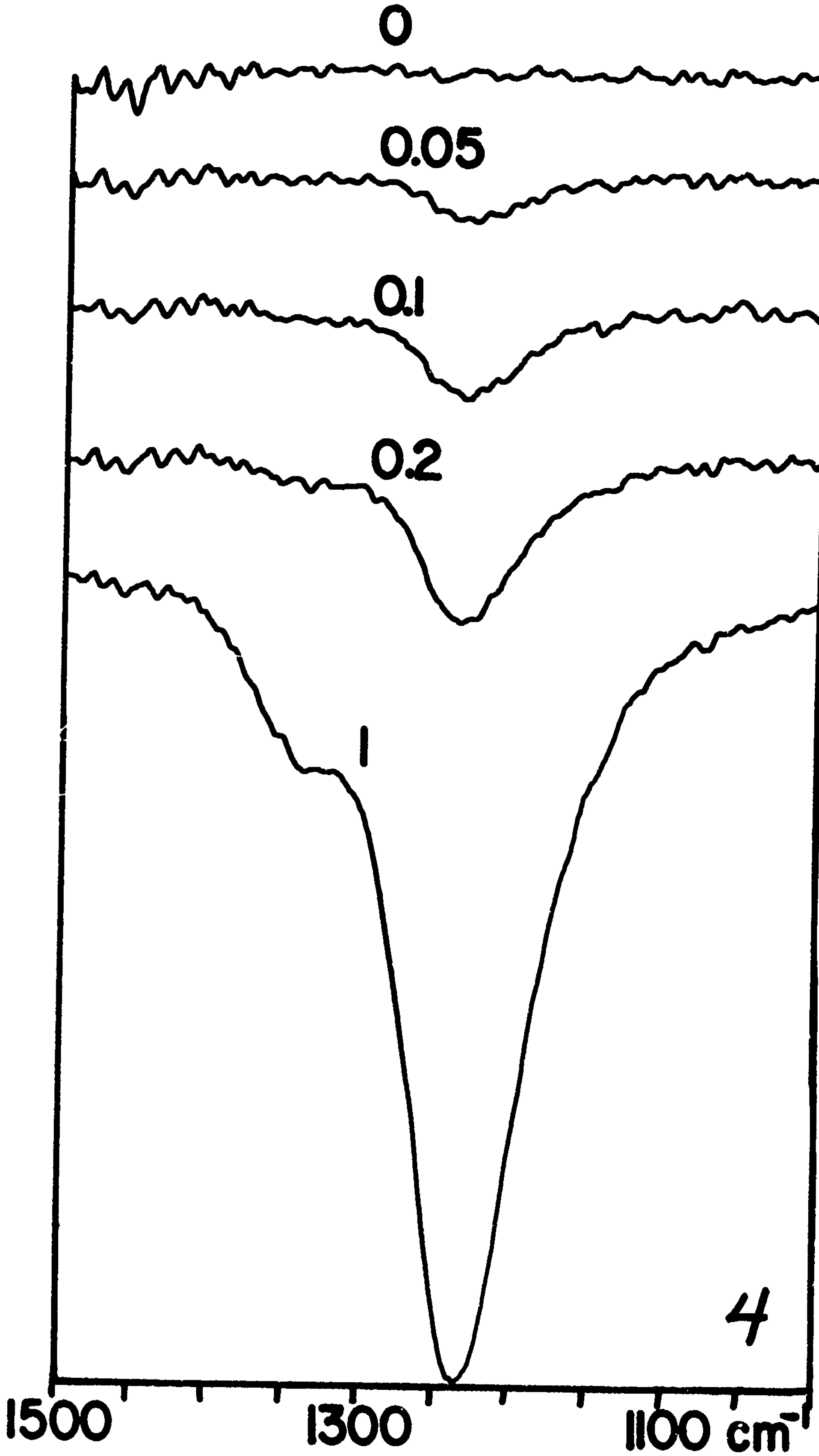
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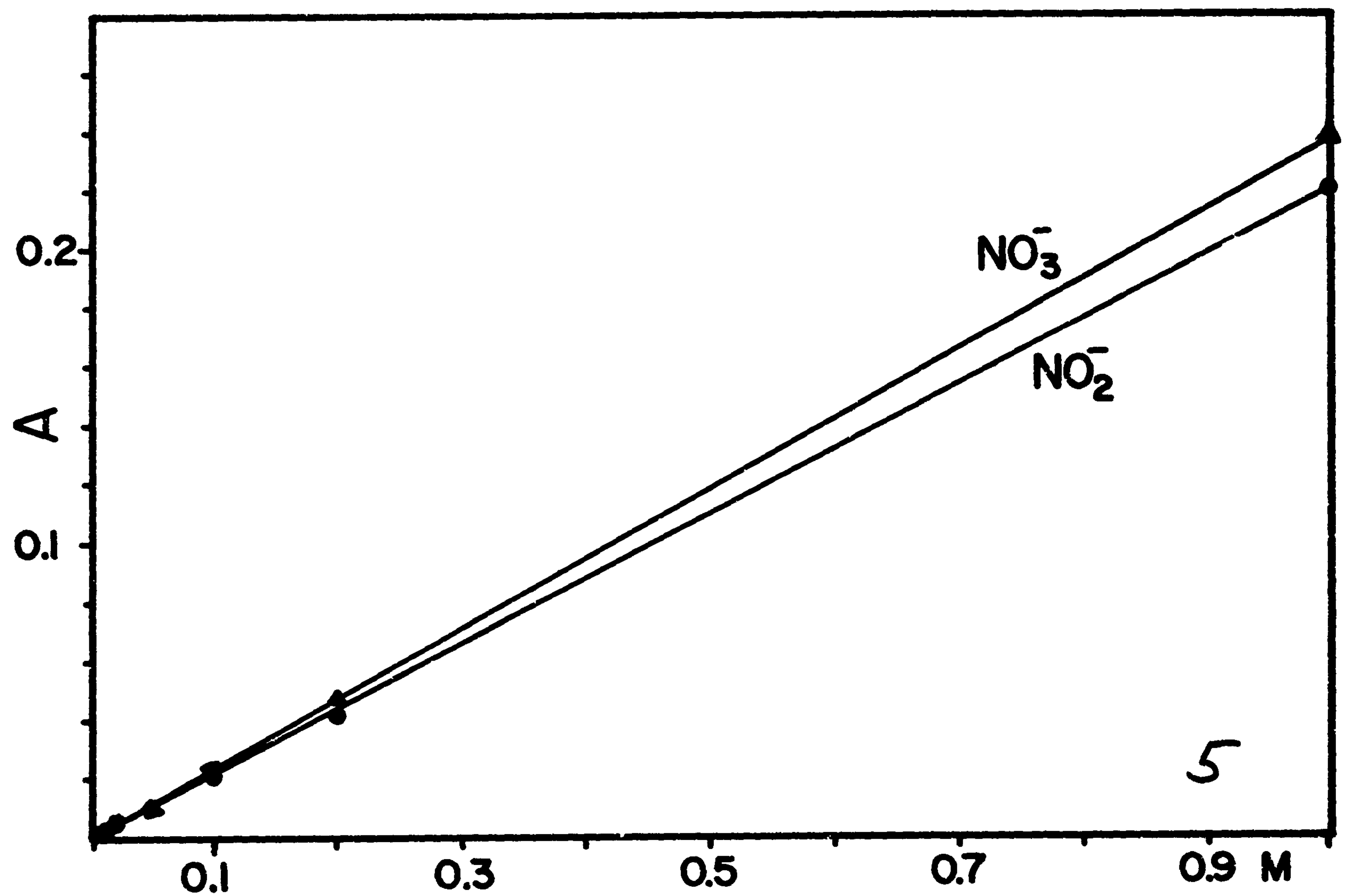

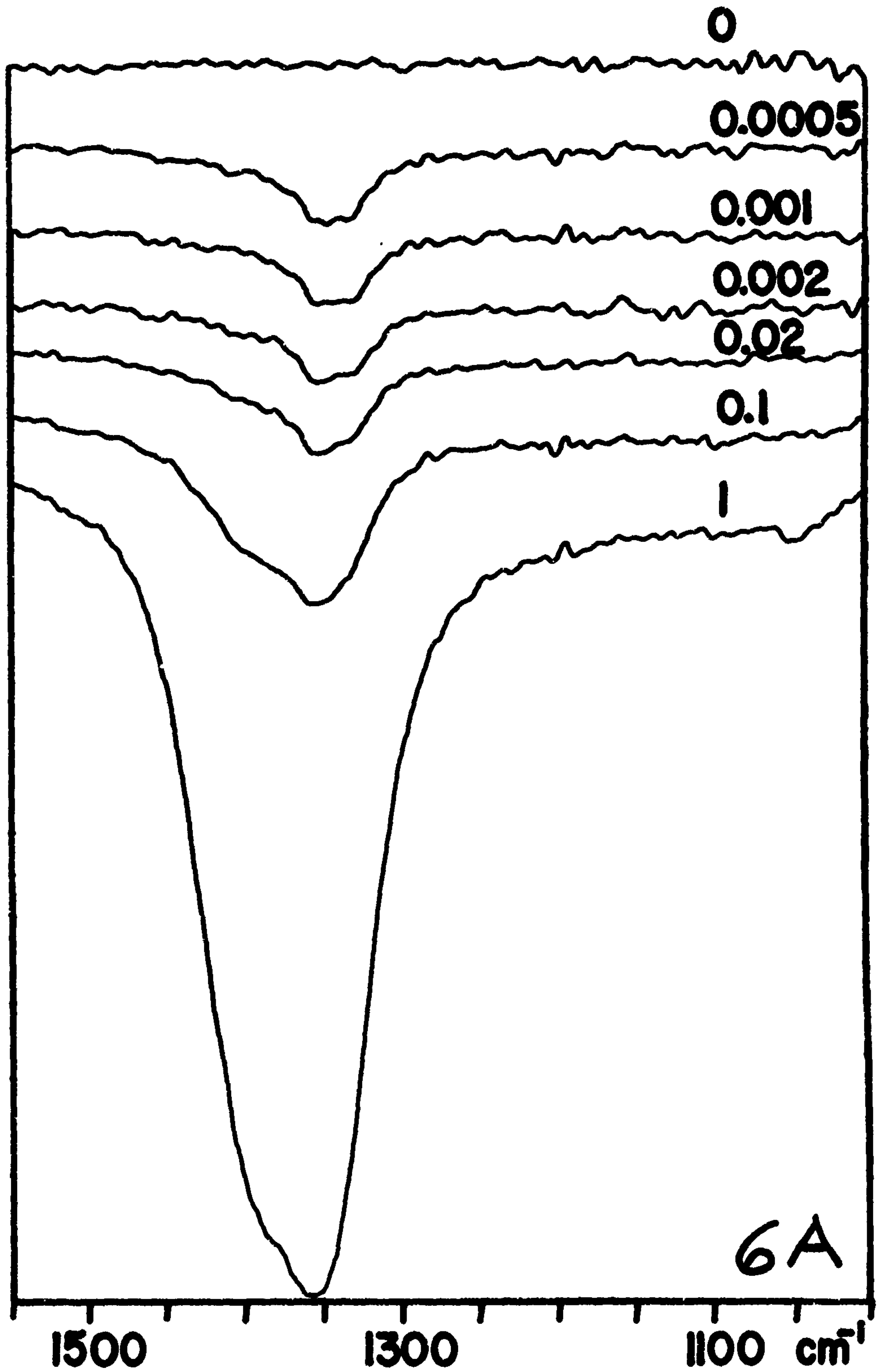
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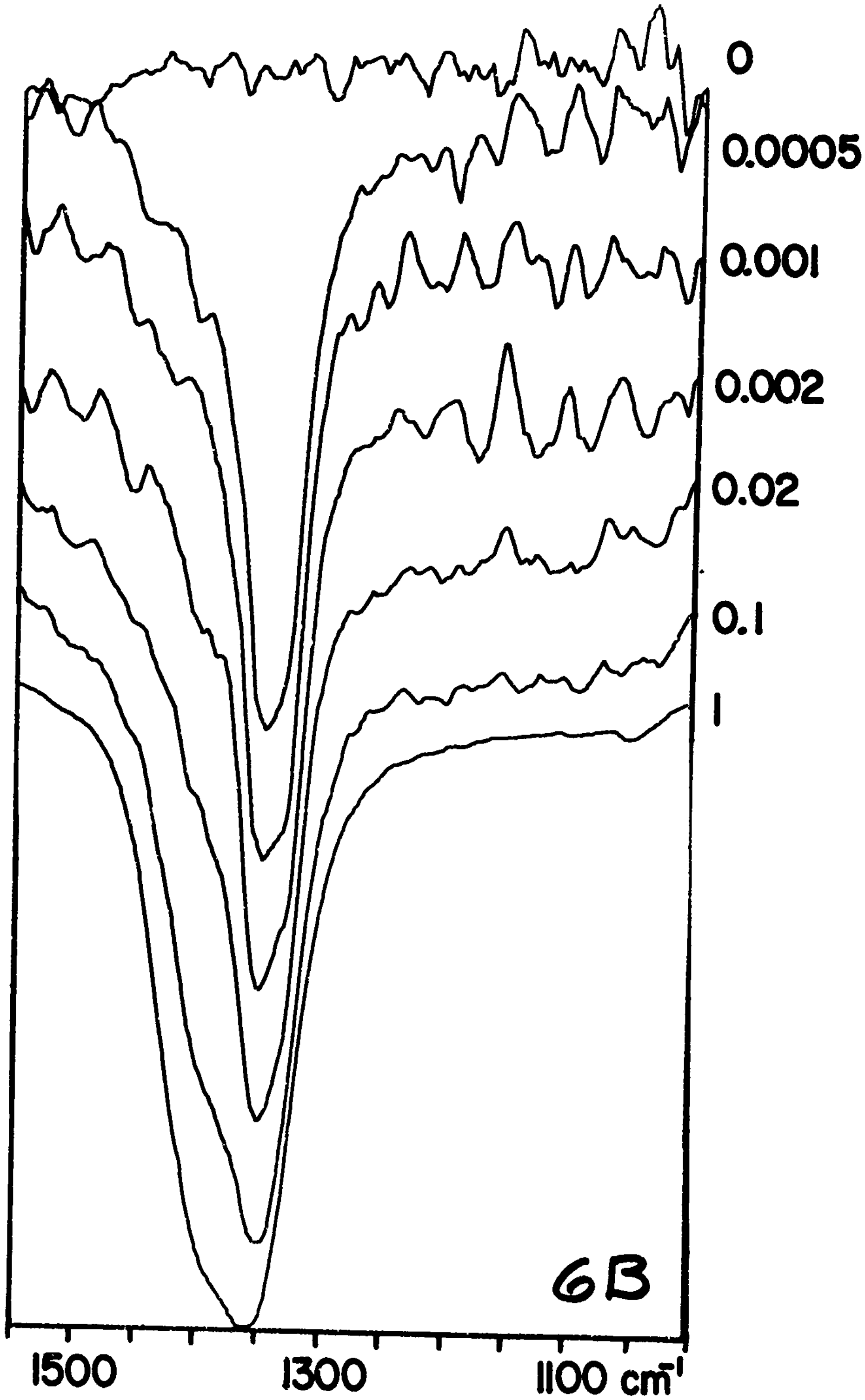

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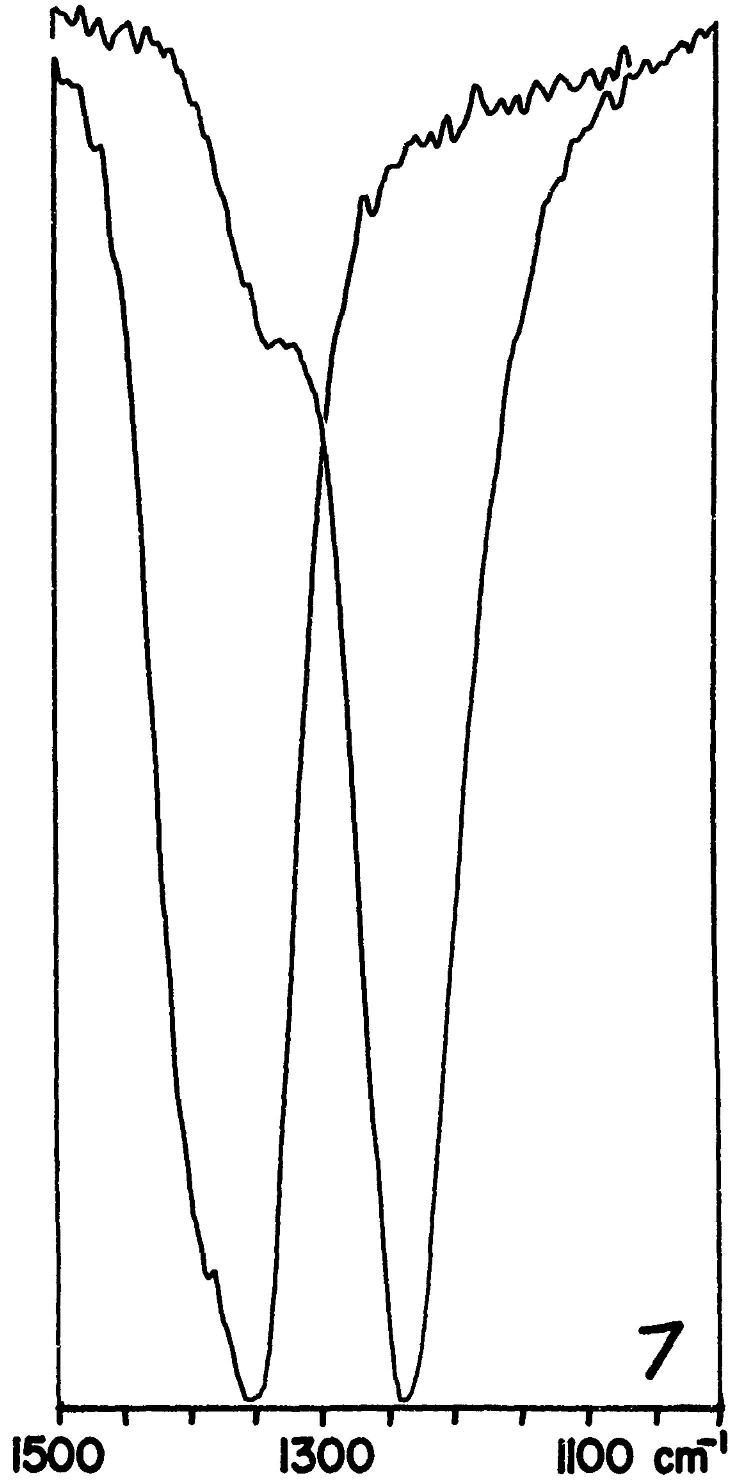
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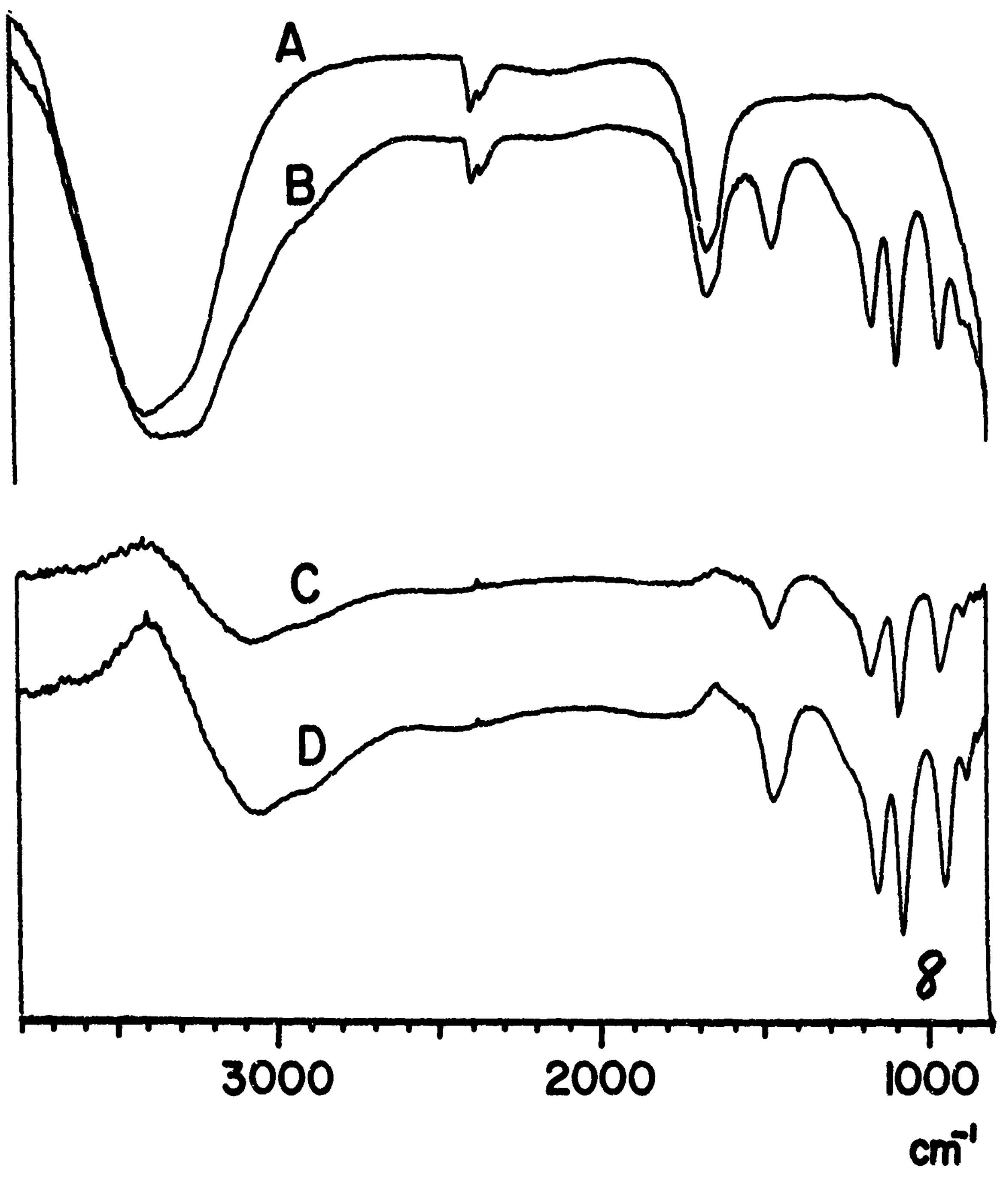

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B
C
D
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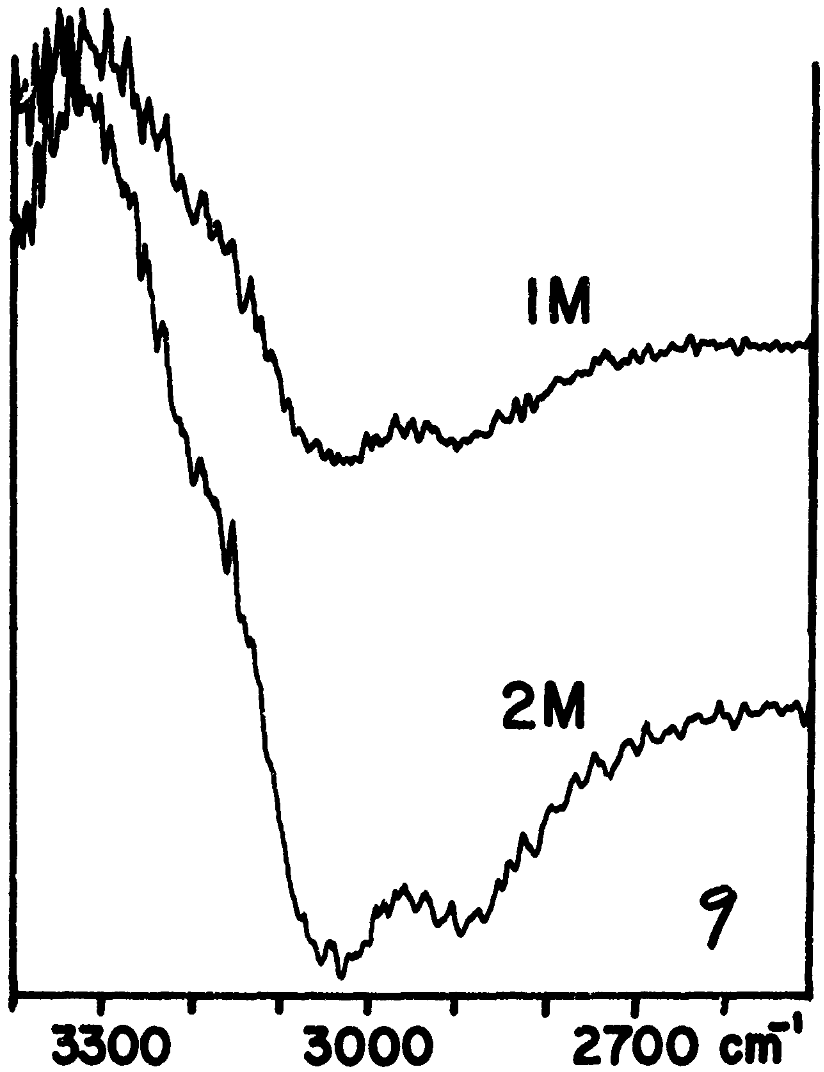
2000
1000
cm⁻¹


1M
2M
9
3300
3000
2700 cm⁻¹